Shell Global Solutions

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To: Melva J. Martin, SCC and Jeff Stevenson, SCC

Subject: 2009 SARA 313 Reporting for the Shell Deer Park Refinery North Effluent Treater ***REVISION 1***[1]

cc: Dan Dobesh, SDPR

This memo summarizes the emission results for the North Effluent Treater (NET) for the Shell Deer Park Refinery (SDPR) for reporting year 2009.

Organic Compound Emissions:

The emissions to air and to water from the North Effluent Treater facilities (NET), as well as the amount abated, were estimated using the data obtained from the 2009 Shell Deer Park Refinery (SDPR) sampling results and from the on-line monitoring system Raddical Insight. For 2009, NET emission calculations were done in two steps due to the system upset that happened in January 2009. Emissions during the upset period were estimated separately. For the rest of the year, the CHEMSETS emissions model named "DP NET 2009_TRI.xls" was used to estimate the emissions. Data inputs included the 2009 annual average flows and concentrations of the listed chemicals. The emissions from the main model run are summarized in Table 1. These are **in addition to** the emissions from the upset period, which were reported in a separate correspondence sent early in 2009 to SDPR environmental personnel.

The CHEMETS model utilized to calculate these emissions was revised in December 2007. Appendix 1 lists the background information including assumptions, data ranges, flow methodology and other pertinent information regarding how these emissions were calculated. It also contains recommendations for improvements in calculations and reporting. These recommendations are summarized in Appendix 2.

The CHEMSETS model DP NET 2009_TRI_R1.xls was run for each chemical on the list to estimate the aqueous effluent concentration and the total NET emissions. The 2009 model output is summarized in spreadsheet "09 Model Output_R1.xls", and in Tables 1 and 2. Historical emission information from 2005 to 2009 have been included in this spreadsheet and Table 2 for comparison purposes. The spreadsheet “ODAS Data 2009_R1.xls” contains the background data and summary of the flows and concentrations of the listed chemicals that were utilized as the inputs for the CHEMSET model.

Ammonia Emissions

The methodology utilized for estimating the ammonia emissions was similar to that utilized for the organic compound emissions. A modified emissions model was used to account for the effect ionization of ammonia has on reducing ammonia volatility. Some of the ammonia

[1] Revised 01/12/10 by BMT. Largest changes are to emissions of MTBE, chloroform and trichloropropane. Corrections were needed to model inputs for DAF / IGF concentrations of noted chemicals.

entering the NET was utilized in the biological treatment process as a nutrient, and some was converted to nitrate via nitrification process. **The information in Table 1 includes the emissions of ammonia from the NET that were calculated by the model.**

Nitrate Emissions

Nitrate was generated in the NET by the biological oxidation of ammonia. Due to its ionic nature, nitrate has no significant emissions to the air. All of the nitrate was discharged in the aqueous effluent.

The 2009 nitrate emissions are summarized in Table 3. These emissions have been based upon the flow weighted nitrate emissions through the treated process wastewater discharge point, R007, and weekly nitrate analysis of that stream. It should be noted that nitrate emissions from 1998 to 2006 are estimates, while 2007 to 2009 are based upon actual sample data.

MTBE Emissions

From 1998 to 2007, NET MTBE emissions were calculated based upon 1998 data. The MTBE unit at the Shell Deer Park Refinery was shutdown prior to the start of 2008, and sample analysis performed in June 2009 confirmed MTBE concentrations substantially below the 1998 levels. These analysis results are shown in the table below. They have been utilized to calculate the 2009 MTBE NET emissions. For the DAF/X-330 emissions, ½ the MDL was utilized in the model per TRI guidelines.

2009 NET Sample Analysis – MTBE

Date of Sample	Time of Sample	Location of Sample	Test America Job Number	Analysis Result		MDL
				ppb	Ppm	ppb
6/10/2009	6:30	X-330	600-11557-10	3.6	0.0036	3.6
6/10/2009	6:00	DAF	600-11557-8	3.6	0.0036	3.6
6/10/2009	6:15	IGF	600-11557-9	595	0.595	3.6

Background Information and Recommendations

Appendix I contains some of the background information for the 2009 emission calculations, recommended changes, updates and suggested reviews for the 2010 reporting year. These recommendations are summarized in Appendix 2.

09 Model Output_R1.xls

ODAS Data 2009_R1.xls

Table 1 2009 NET Emission Estimates and Amounts Abated

Compound Name	Total Influent Loading	Yearly Air Emissions	Discharge in Plant Effluent	Annual Abated
	Pounds/Year			
DICHLORO 2-PROPANOL 1,3	35,002	69	1,555	33,379
ETHYL(2) HEXANOL	0	0	0	0
ACETONE	186,440	55,041	611	130,789
ACETOPHENONE	27,482	1,846	648	24,989
ACETONITRILE	33,669	3,307	1,201	29,160
ALLYL ALCOHOL	22,789	2,504	1,870	18,415
AMMONIA	37,570	589	115	36,866
BENZENE	33,696	362	1	33,334
CHLOROFORM	0	0	0	0
CUMENE (isopropylbenzene)	23,872	17,986	14	5,873
METHYLENE CHLORIDE	18,314	14,814	99	3,402
EPICHLOROHYDRIN	1,133	326	83	724
ETHANOL	35,219	448	477	34,294
DICHLOROETHANE(1,2)	15,047	3,624	182	11,240
GLYCIDOL	2,042	14	153	1,876
ISOBUTYL ALCOHOL	0	0	0	0
PROPANOL ISO	62,625	2,702	5,469	54,454
PROPYL ETHER ISO	1,967	999	10	958
METHANOL	131,312	3,870	4,376	123,066
METHYL ETHYL KETONE	53,265	10,748	1,190	41,327
METHYL ISOBUTYL KETONE	4,745	1,635	3	3,107
BUTANOL-1	0	0	0	0
PHENOL	113,705	103	31	113,571
BUTANOL-s (sec-butyl alcohol; 2-butanol)	12,514	487	1,434	10,592
TOLUENE	31,423	847	1	30,575
TRICHLOROPROPANE(1,2,3)	0	0	0	0
PROPANOL	90,791	2,510	5,993	82,289
PENTANES [n-pentane]	0	0	0	0
PENTANES [isopentane]	0	0	0	0
HEXANE(-n)	0	0	0	0
HEXANE(-n) [C6 saturates (non-hexane)]	0	0	0	0
HEPTANE(-n) [C7 Saturates]	0	0	0	0
OCTANE [C8 saturates]	0	0	0	0
C9+ ALKANES	0	0	0	0
C9 AROMATICS	0	0	0	0
ETHYLBENZENE	0	0	0	0
METHYL-TERT-BUTYL ETHER	2,071	361	32	1,678
XYLENE(-o)	0	0	0	0
BUTANE	0	0	0	0
DICHLORO PROPANOL 2,3	92,887	3,298	3,634	85,955
DIACETONE ALCOHOL	1,476	2	6	1,469
hydroxyacetone (hydroxy DMK)	2,210	4	20	2,186
MESITYL OXIDE	3,986	147	11	3,828
METHYL ISOBUTYL CARBINOL	1,046	552	0	493
BUTYRALDEHYDE	0	0	0	0
CYCLOHEXANE [C6 Napthenes]	0	0	0	0
METHYL CYCLOHEXANE [C7 Naphthenes]	0	0	0	0
Hexylene Glycol	144,512	2	144,509	2
TOTALS	1,222,812	129,194	173,729	919,889

Table 2. NET Emissions Comparison - 2004 through 2009

Compounds Name	2005 Emission	2006 Emission	2007 Emission	2008 Emission	2009 Emission
	Pounds per year	Pounds per year	Pounds per year	Pounds per year	Pounds per year
	Utilized 1/2 Method Detection Limit (MDL) for non-detect and less than MDL sample analysis				
DICHLORO 2-PROPANOL 1,3	17	95	137	84	69
ETHYL(2) HEXANOL	0	0	0	0	0
ACETONE	39,710	37,069	43,777	37,036	55,041
ACETOPHENONE	168	423	171	1,906	1,846
ACETONITRILE	2,637	1,923	3,698	2,908	3,307
ALLYL ALCOHOL	107	114	199	955	2,504
AMMONIA	1,307	1,683	1,166	809	589
BENZENE	3,951	1,537	934	610	362
CHLOROFORM	8,183	10,323	5	5	0
CUMENE (isopropylbenzene)	8,032	1,736	9,074	15,610	17,986
METHYLENE CHLORIDE	17,796	13,850	3,109	20,459	14,814
EPICHLOROHYDRIN	307	297	366	2,492	326
ETHANOL	598	537	2,091	589	448
DICHLOROETHANE(1,2)	1,081	88	3,260	702	3,624
GYLCIDOL	14	8	11	70	14
ISOBUTYL ALCOHOL	0	0	0	0	0
PROPANOL ISO	3,064	3,211	3,706	1,948	2,702
PROPYL ETHER ISO	3,436	1,235	4,776	6,783	999
METHANOL	8,618	2,652	5,106	2,474	3,870
METHYL ETHYL KETONE	6,163	9,104	6,132	7,250	10,748
METHYL ISOBUTYL KETONE	667	768	1,194	6,636	1,635
BUTANOL-1	0	0	0	0	0
PHENOL	21	40	121	80	103
BUTANOL(S)	474	518	938	835	487
TOLUENE	747	5,061	20,673	9,029	847
TRICHLOROPROPANE(1,2,3)	148	435	0	0	0
PROPANOL	323	6,945	385	2,326	2,510
PENTANES	0	0	0	0	0
PENTANES	0	0	0	0	0
HEXANE(-n)	0	0	0	0	0
HEXANE(-n)	0	0	0	0	0
HEPTANE(-n)	0	0	0	0	0
OCTANE	0	0	0	0	0
C9+ ALKANES	0	0	0	0	0
C9 AROMATICS	0	0	0	0	0
ETHYLBENZENE	0	0	0	0	0
METHYL-TERT-BUTYL ETHER	27,481	33,715	30,707	312	361
XYLENE(-o)	0	0	0	0	0
BUTANE	0	0	0	0	0
DICHLORO PROPANOL 2,3	107	404	615	4,590	3,298
DIACETONE ALCOHOL	1	1	4	8	2
hydroxyacetone (hydroxy DMK)	4	11	5	30	4
MESITYL OXIDE	117	121	145	1,117	147
METHYL ISOBUTYL CARBINOL	480	497	580	4,439	552
BUTYRALDEHYDE	0	0	0	0	0
CYCLOHEXANE	0	0	0	0	0
METHYL CYCLOHEXANE	0	0	0	0	0
HEXYLENE GLYCOL	0.067	0.2	0	0	2
Totals:	**135,758**	**134,400**	**143,086**	**158,492**	**129,223**

Table 3. NET Nitrate Emissions Estimated and Measured – 1998 to 2009

Year	R007 Annual Average Flow Rate	Estimated NO3 in Effluent	Measured NO3 in Effluent	Calculated NO3 in Effluent	Measured NO3 in Effluent
	GPM	lbs NO_3 / Year	lbs NO_3 / Year	mg/L	mg/L
1998	4,200	2,074,132		112.7	
1999	4,400	2,258,896		117.2	
2000	4,786	802,356		38.3	
2001	4,585	902,621		44.9	
2002	4,815	825,319		39.1	
2003	4,748	1,125,195		54.1	
2004	4,654	1,586,800		77.8	
2005	4,245	1,311,553		70.5	
2006	4,609	1,632,317		80.9	
2007	5,207		1,190,485		52.13
2008	4,839		1,628,782		76.55
2009	**3,874**		**939,772**		**55.36**

Appendix 1. Background Information

1.1) NET Flow Rates

a. NESHAP stream flow rate

i) For 2009, the NESHAP stream flow rate was taken from Raddical View point IGF_FLOW_NET@dprcalc.

b. CCLP, TC&G and DD2 CPI flow rates in DAF stream

i) Early in 2001, a project intercepting the dry weather flow to North Pond was implemented. As a result, the three CPI (CCLP, TC&G and DD2) flow rate measurement systems were no longer valid. The measured flow rates were extremely high and did not match the total flow at the DAFs which are located downstream of the three CPIs.

ii) To obtain the individual flow rates of the three CPIs, the total flow at the DAF was utilized. The DAF flow was proportionally split based upon the ratios of the three CPI flow rates during 2000.

iii) **Recommendation:** The flow rates and proportional split for the individual CPI's, Manhole #4, and DAF need to be reviewed based upon flow monitoring conducted in 2007 during the Source Control Study. The proportional split and flow rate calculation methodology should then be updated based upon the review conclusions.

c. Outfall R007 Flow Rate

i) The sum of the DAF and IGF flows should equal the combined rates for Outfall R007 and the return fire water flow. For reporting year 2009, the combined measured flow rate for Outfall R007 and the fire water return was 4,440 gpm daily annual average, while the daily annual average sum of flows from the DAF and IGF systems was 4,720 gpm (about 6.4% difference). This represents a marked improvement in agreement from previous years.

ii) For reporting year 2009, the DAF and IGF flow rates were utilized for the emission calculations.

iii) The R007 flow rate was taken from Radical View point NET.FI237A.

1.2) Laboratory Testing Results

a. In 2007, Radical View organic analysis data for chloroform and trichloropropane analysis for the IGF, DAF and X330 sump was determined to be inaccurate by SDPR. SDPR determined that the peaks shown by the primary analytical method were not, in fact, these compounds. This was determined by a second analytical method. This change was documented in a January 8, 2008 email correspondence between SGSUS GSRU and SDPR personnel.. A reading of 1 x E^{-07} was entered into the emissions model for each of these compounds at the DAF. This was done to ensure that the emission calculation model ran properly.

i) Recommendation: Since chloroform and trichloropropane are not present in refinery waste water, and it has been determined that the analytical results are inaccurate, remove these compounds from the IGF, DAF and X330 sump analysis schedule.

b. For those points where no 2009 laboratory testing results were available, a reading of 1 x E^{-07} was entered. This was done to ensure that the emission calculation model ran properly.

c. Based upon the TRI reporting guidelines, one-half of the method detection limit (MDL) was used in the emission calculation for reporting year 2009 for all those compounds that had analytical results below detection limits. The method detection limits utilized are listed below.[2]

Compound	Method Detection Limit (mg/L)	½ Method Detection Limit (mg/L)
Benzene	0.01	0.005
Cumene	1.4	0.7
Dichloromethane	1.4	0.7
Ethylene dichloride	0.01	0.005
MTBE	0.0036	0.0018
Organic Compounds (not listed above)	0.1	0.05

d. In 2009, analysis of the benzene and ethylene dichloride content was done for the X330 sump but not the DAF. For emission calculation purposes, the X330 analysis results were used for the DAF in the emissions model.

i) **Recommendation:** Determine if analysis for benzene and ethylene dichloride at the DAF sample point would be more appropriate than the X330 sump for calculating emissions from this portion of the NET system. Based upon the results of this analysis, update the sampling requirements at the DAF and X330 sump.

e. The following parameters did not show any analytical results for 2009 for either the DAF or IGF:

Compound Number	Compound Name
190	ETHYL(2) HEXANOL
222	ISOBUTYL ALCOHOL
60	BUTANOL-1
384	PENTANES [n-pentane]
384	PENTANES [isopentane]
210	HEXANE(-n)
210	HEXANE(-n) [C6 saturates (non-hexane)]
204	HEPTANE(-n) [C7 Saturates]
266	OCTANE [C8 saturates]
383	C9+ ALKANES
382	C9 AROMATICS
182	ETHYLBENZENE
361	XYLENE(-o)
381	BUTANE
363	BUTYRALDEHYDE
113	CYCLOHEXANE [C6 Napthenes]
233	METHYL CYCLOHEXANE [C7 Naphthenes]

i) **Recommendation:** Document in TRI background material why sample analysis is not being run on these compounds.

[2] Method detection limits per 12/19/08 email from Melva Martin, SCC.

f. MtBE concentration

i) In 2009, sample analysis of various NET inlet flows (X330, DAF, IGF) resulted in updated MTBE concentrations. These concentrations were utilized for the 2009 calculations.

g. Ammonia Calculations

i) After 7/20/01, ammonia was not measured in the DAF composite sample. In this report, the ammonia concentration at the DAF unit was estimated using the annual average value of X330 sump ammonia measurements. The X330 sump is located upstream of the DAF unit.

ii) The ionization of ammonia within the system is being calculated utilizing an estimate of the Trickling Filter waste water pH.

iii) **Recommendation:** To ensure more accurate ammonia reporting, periodic monitoring of the Trickling Filter waste water pH should be instituted.

h. Nitrate Emissions

i) In 2007, the refinery began routine sampling and analysis of the R007 effluent for nitrate emissions from R007. The 2007 through 2009 results differ from previous years in that the emissions are based on actual nitrate sample results rather than being a calculated number.

ii) Nitrate enters the refinery in the raw river water that is treated to produce process water. Per TRI reporting requirements, the amount of nitrate being discharged through R007 may be reduced by the amount of nitrate in the refinery process water system that ends up in the NET. Currently, the amount of nitrate in the raw water is unknown due to lack of sample data.

iii) **Recommendation:** In 2010, institute regular sampling and analysis of the raw water entering the refinery for nitrate content and utilize this information to net out the nitrate amount exiting the refinery through R007.

i. **Recommendation:** The sample points and organic compounds monitored should be reviewed, and updates initiated based upon the conclusions of the review.

1.3) **Data Range:** The data range utilized for reporting year 2009 was January 1, 2009 to December 31, 2009.

1.4) SARA 313 NET Emissions – Emission Report Model and Procedure

a. 2009 Model Updates

i) None made for this model run.

b. The NET Chemsets Emission Model has had only minor updates and verification since the 1990's.

i) **Recommendation:** Verify that the current conditions at the NET are accurately reflected in the CHEMSETs model. This would include review of the existing NET flow path, waste water stream flow rate assumptions, chemical concentrations, and basic equipment information. This work would include walking the unit, analytical testing of key parameters to verify model calculations, and updating the model to reflect any changes.

c. SARA 313 NET Procedure

i) The procedure being utilized to prepare this report is incomplete and outdated.

ii) **Recommendation:** The development of a formalized procedure that documents TRI report preparation including Raddical View points, assumptions, calculations, and final report preparation should be done. The starting basis would be the existing Mark Yin procedure that was last revised in 2004. This would provide continuity and consistency for changes in personnel preparing the report, and would also provide backup for any

questions regarding data preparation and results. This would also facilitate turnover of NET TRI report preparation to Shell Deer Park personnel.

Appendix 2. Recommendation Summary

2.1) The flow rates and proportional split for the individual CPI's, Manhole #4, and DAF need to be reviewed based upon flow monitoring conducted in 2007 during the Source Control Study. The proportional split and flow rate calculation methodology should then be updated based upon the review conclusions.

2.2) The sample points and organic compounds monitored should be reviewed, and updates initiated based upon the conclusions of the review. This should include:

- **a.** Determination if analysis for benzene and ethylene dichloride at the DAF sample point would be more appropriate than the X330 sump for calculating emissions from this portion of the NET system.
- **b.** Remove chloroform and trichloropropane from the DAF, IGF and X330 sump analysis schedule.
- **c.** Document in TRI background material why sample analysis is not being run on organic compounds shown in 1.2.e.

2.3) Institute periodic monitoring and documentation of the Trickling Filter waste water pH.

2.4) In 2010, institute routine sampling and analysis of the raw water entering the refinery for nitrate content and utilize this information to net out the nitrate amount exiting the refinery through R007.

2.5) Verify that the current conditions at the NET are accurately reflected in the CHEMSETs model. This would include review of the existing NET flow path, waste water stream flow rate assumptions, chemical concentrations, and basic equipment information. This work would include walking the unit, analytical testing of key parameters to verify model calculations, and updating the model to reflect any changes.

2.6) The development of a formalized procedure that documents TRI report preparation including Radical View points, assumptions, calculations, and final report preparation should be done. The starting basis would be the existing Mark Yin procedure that was last revised in 2004. This would provide continuity and consistency for changes in personnel preparing report, and would also provide backup for any questions regarding data preparation and results. This would also facilitate turnover of NET TRI report preparation to Shell Deer Park personnel.